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INTERACTIONS OF STACK GAS SULFUR AND NITROGEN OXIDES ON DRY SORBENTS

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National Environmental Research Center
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ABSTRACT

It was noted that the standard analytical system used for the measurement of NO emissions gave incorrect NO concentrations in the presence of SO_2. The problem was traced to the dry sorbents used to remove water vapor prior to the NO analysis. A brief test series demonstrated that both Drierite and molecular sieve sorbents can cause incorrect NO results if SO_2 is present. Further testing revealed that the materials are capable of simultaneous removal of both NO and SO_2 even in low concentrations. More work is needed to define the actual fate of these species; however, it appears that this might offer a possible NO_x/SO_x control technique since the data indicate that the sorbent effect is thermally regenerable.

CONTENTS

	Page
Abstract	iii
List of Figures	v
List of Tables	v
Introduction	1
Isothermal Testing with Known Gas Concentrations	3
Hot-Flow Testing -- Propane Combustion Doped with SO_2	7
Hot-Flow Testing -- Residual-Oil-Fired Package Boiler	13
Conclusions/Recommendations	17
Bibliography	18

FIGURES

No.		Page
1	Isothermal Test Facility	4
2	Hot-Flow Test Facility	8
3	Recorded Traces for Tests B-1, B-5, B-7, and B-8	11
4	Package Boiler Hot-Flow Test Facility	12
5	Emission Reduction Across a 65-Gram Molecular Sieve Bed	16

TABLES

No.		Page
1	Series 1 Results	5
2	Series 2 Results	9
3	Series 3 Results -- Fmissions After 5 Minutes of Sampling	14

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INTRODUCTION

During recent experimental testing, the Combustion Research Section (CRS) of EPA's Control Systems Laboratory observed that sampling and analytical procedures previously utilized for measuring NO_x emissions from natural gas and light oil combustion[1] were not satisfactory for measuring nitrogen oxides (NO_x) in sulfur oxide (SO_x) laden gases. For example, sulfur dioxide (SO_2) levels of 1600 ppm (equivalent of 2.5 percent sulfur fuel) resulted in measured NO_x concentrations of less than half the actual level. The problem was finally isolated to the dry sorbent system used to remove water from the gas sample prior to the analytical instrumentation.

It is well known (e.g., Sundaresan et al.)[2] that certain drying materials such as commercial zeolites and silica gel have the ability to selectively adsorb NO_x from nitric acid tail gases where the NO_x concentration is in excess of 2000 ppm. Previous CRS work had shown that NO adsorption and/or reaction did not occur with the molecular sieve and Drierite drying agents utilized in the standard CRS analytical train;[1] however, all prior work had been done with essentially sulfur free flue gases. The purpose of the work reported herein was to briefly investigate the observed SO_x/NO_x/drying agent interactions and to define what further work, if any, should be done in the area.

A three part approach was utilized. First, controlled mixtures of ambient air, nitric oxide (NO), and SO_2 were prepared, passed through various types of drying systems, and then sampled to determine exactly what interferences and/or interactions should be expected. Next, the tests were repeated using actual flue gas from a propane flame with and without SO_2 present. Finally, the work was extended to full scale testing on a package boiler burning residual oil with 0.9 percent sulfur.

ISOTHERMAL TESTING WITH KNOWN GAS CONCENTRATIONS

Under combustion conditions it is not possible to measure the amount of NO in a given flue gas stream without first removing the water of combustion. (Failure to do so will result in water vapor condensation in the sample cell and/or instrument interference.) Therefore, in the first test series ambient air (with appropriate NO and SO_2 added) was utilized instead of actual flue gas so that the sample could be run directly to the appropriate analyzer. The purpose of this series was to define which elements if any of the standard drying system needed further investigation.

The experimental facility used for this test series is shown in Figure 1. Basically, it was designed to allow sampling a gas flow of ambient air with and without NO and/or SO_2. Both the NO and SO_2 came from laboratory cylinders through precalibrated rotameters into the sampling duct ahead of the mixing section. Sampling was accomplished via a standard quartz combustion probe. From the probe the sample went either directly to the analyzer (baseline tests) or to the system component being checked (e.g., the ice bath) then to the analyzer. All NO analysis in this series was done with a chemiluminescent analyzer.

The results of these tests are shown in Table 1. In Tests A-1 through A-5 the stream being sampled contained only ambient air and approximately 200 ppm NO. As the data indicate, none of the common drying schemes had any significant effect on the measurement. In Tests A-6 through A-10 sufficient SO_2 was added to the air stream to give about 1600 ppm in the mixture. As the data indicate both the Drierite and the molecular sieve led to radical reductions in the measured NO level initially; however, with time both appeared to "saturate" and the NO asymptotically approached the correct value. These data suggest that some type of NO_x/SO_x

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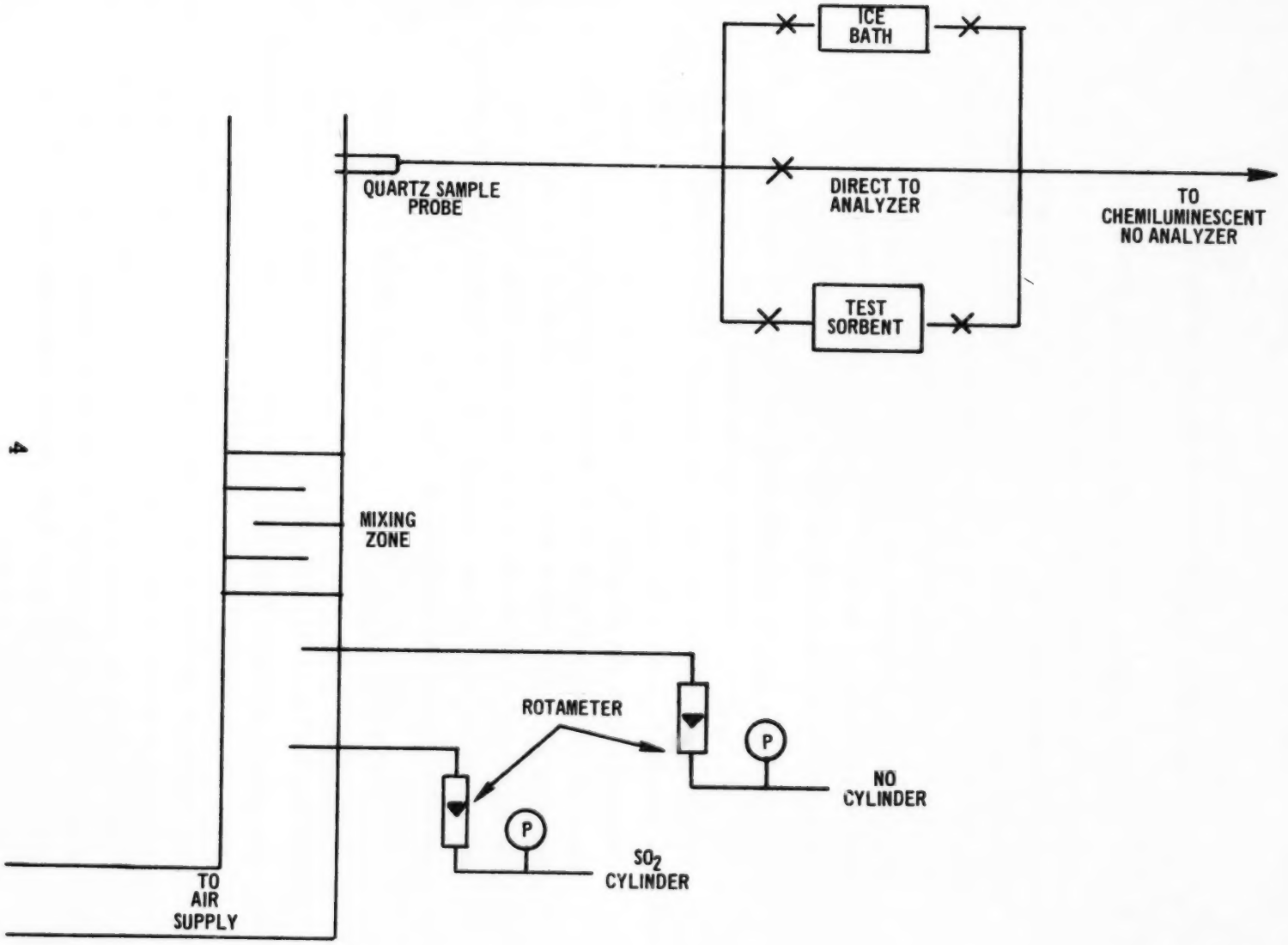

Figure 1. Isothermal test facility.

Table 1. SERIES 1 RESULTS

Test No.	Test gas composition	Sample conditions[a]	Chemiluminescent measured NO, ppm
A-1	Ambient air + ≈200 ppm NO	Direct to analyzer	194
A-2	"	Drierite,[b] 15 g[c]	204
A-3	"	Molecular sieve,[d] "	189
A-4	"	$CaCl_2.2H_2O$,[e] "	195
A-5	"	Ice bath	193
A-6	Ambient air + ≈200 ppm NO + ≈1600 ppm SO_2	Direct to analyzer	184
A-7	"	Drierite, 15 g	(2 min.) 141, (10 min.) 176
A-8	"	Molecular sieve, "	(2 min.) 67, (10 min.) 159
A-9	"	$CaCl_2.2H_2O$, "	185
A-10	"	Ice bath	183
A-11	Ambient air + ≈1600 ppm SO_2	Direct to analyzer	0.98
A-12	"	Drierite, 15 g	0.60
A-13	"	Molecular sieve, "	0.25
A-14	"	$CaCl_2.2H_2O$, "	0.78
A-15	"	Ice bath	0.95

[a]Total sample flow was 71 liters/hr (2.5 scfh). The flue gas sample flowed through a particulate filter to prevent clogging instrument sampling lines. (There was no evidence that this filter adversely affected measured NO_x readings.) A dry layer air filter pack #99/97 Microsorban made by Delbag Co. was used to remove particulates.

[b]New "Drierite" - anhydrous $CaSO_2$, W. A. Hammond Drierite Co.

[c]Fresh drying agent materials were weighed on a triple-beam balance for each sample requiring an agent.

[d]New molecular sieve - #022-006-3A, #1 pellet, Guild Corp. (clay base).

[e]$CaCl_2.2H_2O$ - Calcium chloride, reagent grade, Matheson, Coleman & Bell.

interaction was occurring; however, unfortunately during this series it was not possible to measure SO_2 to determine its fate. It was also noted, that if the bulk of the flow (the ambient air) was replaced by pure nitrogen no NO/SO_2 interaction was observed. This suggests that O_2 and/or water vapor was also involved.

In Tests A-11 through A-15 the NO was turned off to investigate possible negative interference effects by SO_2 on the analyzer and the system components. As the data show SO_2 had essentially no positive or negative effect on the chemiluminescent NO analyzer since all readings were less than 1 ppm. The data do show, however, that even at the ambient level of about 1 ppm NO, molecular sieve and Drierite reduced the NO in the presence of SO_2.

HOT-FLOW TESTING -- PROPANE COMBUSTION DOPED WITH SO_2

In the second test series flue gas from propane combustion was artificially doped with SO_2 on a controlled basis. The purpose of this series was to investigate the NO_x/SO_x interaction on as nearly a practical system as possible and still be able to control the SO_2 concentration in the flue gas stream being sampled. Figure 2 shows the test facility used for this portion of the work. Basically, it was an upright multi-fuel combustor, with a 40.6 cm (16-in.) ID refractory combustion chamber, and hot-air heat exchanger. Combustion air was supplied by several air blowers in a variety of combinations so that ambient air, preheated air, or flue gas can be supplied to the primary, axial, or swirl streams. The combustor, burner, and support facilities were identical to those used in previous studies.[3] In this series a six-hole radial propane injector was utilized and the combustor was fired at 75 million cal/hr (300,000 Btu/hr) and 5 percent excess air.

The NO in this test series was the result of the normal propane combustion (as compared to the first test series where with no flame the NO level was simulated by injection of concentrated NO). The SO_2 was injected after the combustion zone to prevent flame zone reactions and at a flow to give a concentration of 1600 ppm inside the combustor. As before NO was measured with a chemiluminescent analyzer. Instrumentation was not available for SO_2.

The results of this test series are presented in Table 2. In tests B-1 through B-4 the only major pollutant in the flue gas being sampled was NO (since propane contains no sulfur and this

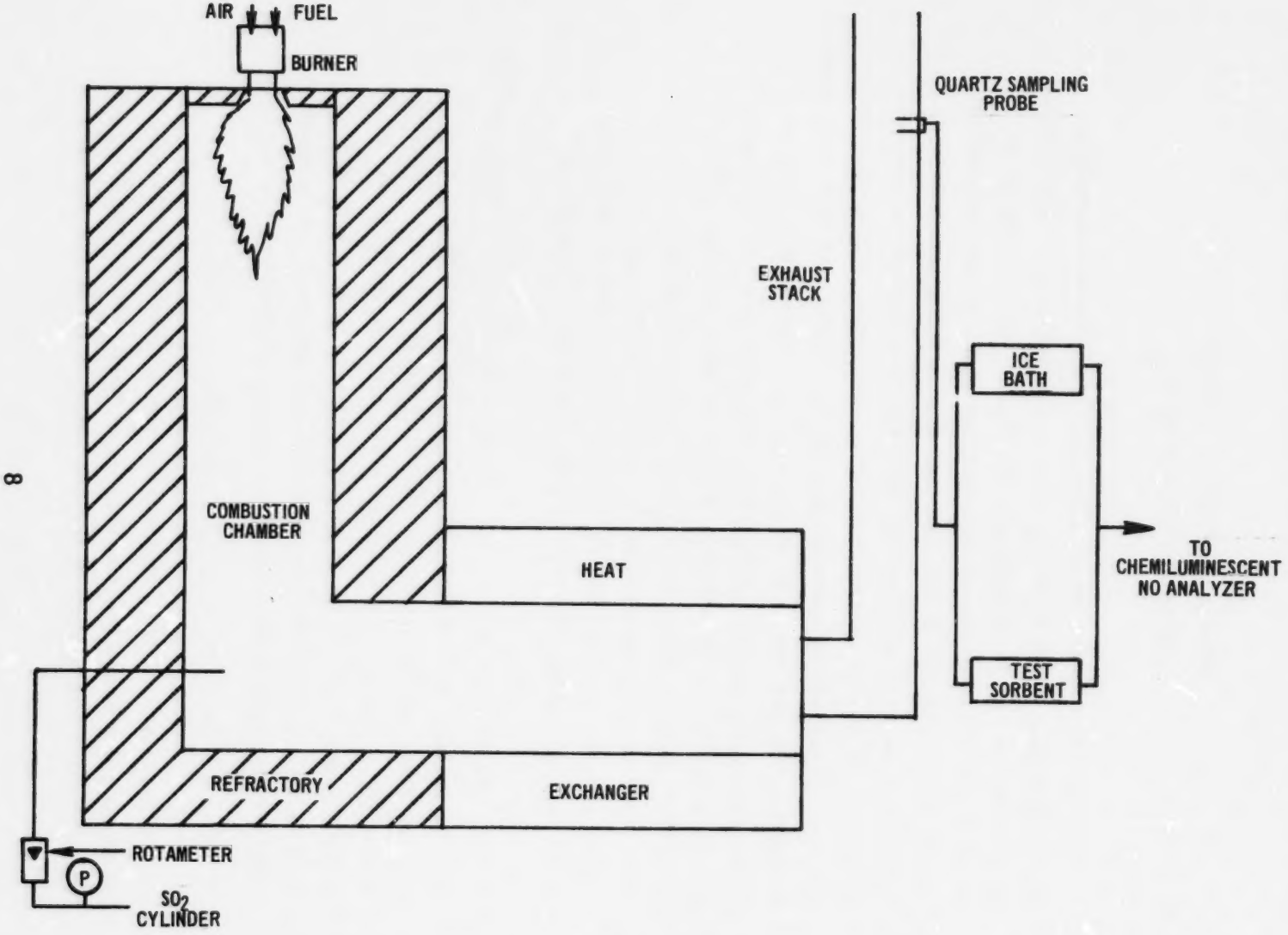

Figure 2. Hot-flow test facility.

Table 2. SERIES 2 RESULTS

Test No.	Test gas composition	Sample conditions[a]	Chemiluminescent measured NO, ppm
B-1	Combustion gas	Ice bath	94
B-2	"	Drierite,[b] 15 g[c] + ice bath	96.5
B-3	"	Molecular sieve,[d] " "	98.5
B-4	"	$CaCl_2.2H_2O$,[e] " "	94
B-5	Combustion gas + ~1600 ppm SO_2	Ice bath	94
B-6	"	Drierite, 15 g[c] + ice bath	(2 min.) 41, (30 min.) 89
B-7	"	Molecular sieve " "	(2 min.) 33, (30 min.) 92
B-8	"	$CaCl_2.2H_2O$, " "	94

[a]The total sample flow was 71 liters/hr (2.5 scfh). In all cases the flue gas sample flowed through a particulate filter to prevent clogging the instrument sampling lines. (There was no evidence that this filter had any adverse effect on measured NO_x readings.) A dry layer air filter pack #99/97 Microsorban made by Delbag Co. was used to remove particulates.

[b]New "Drierite" - anhydrous $CaSO_4$, W. A. Hammond Drierite Co.

[c]Fresh drying agent materials were weighed out on a triple beam balance for each sample where an agent was required.

[d]New molecular sieve - #022-006-3A, #1 pellet, Guild Corp. (clay base).

[e]$CaCl_2.2H_2O$ - Calcium chloride, reagent grade, Matheson, Coleman & Bell.

combustor does not produce significant carbon monoxide, unburned hydrocarbons, or NO_2). As in the first test series all of the drying methods gave essentially the same NO concentration level; there was no evidence of any unusual interactions. (The sample could not be run directly to the analyzer without the ice bath due to water condensation in the analyzer cell.)

During Tests B-5 through B-8, SO_2 was added to the flue gas stream and as before the use of both Drierite and molecular sieve gave incorrect NO readings. Figure 3 shows the recorder traces for the $CaCl_2$ and molecular sieve tests. As these data indicate 15 grams of molecular sieve material required almost 30 minutes before equilibration occurred, while the $CaCl_2.2H_2O$ gave the correct reading almost immediately.

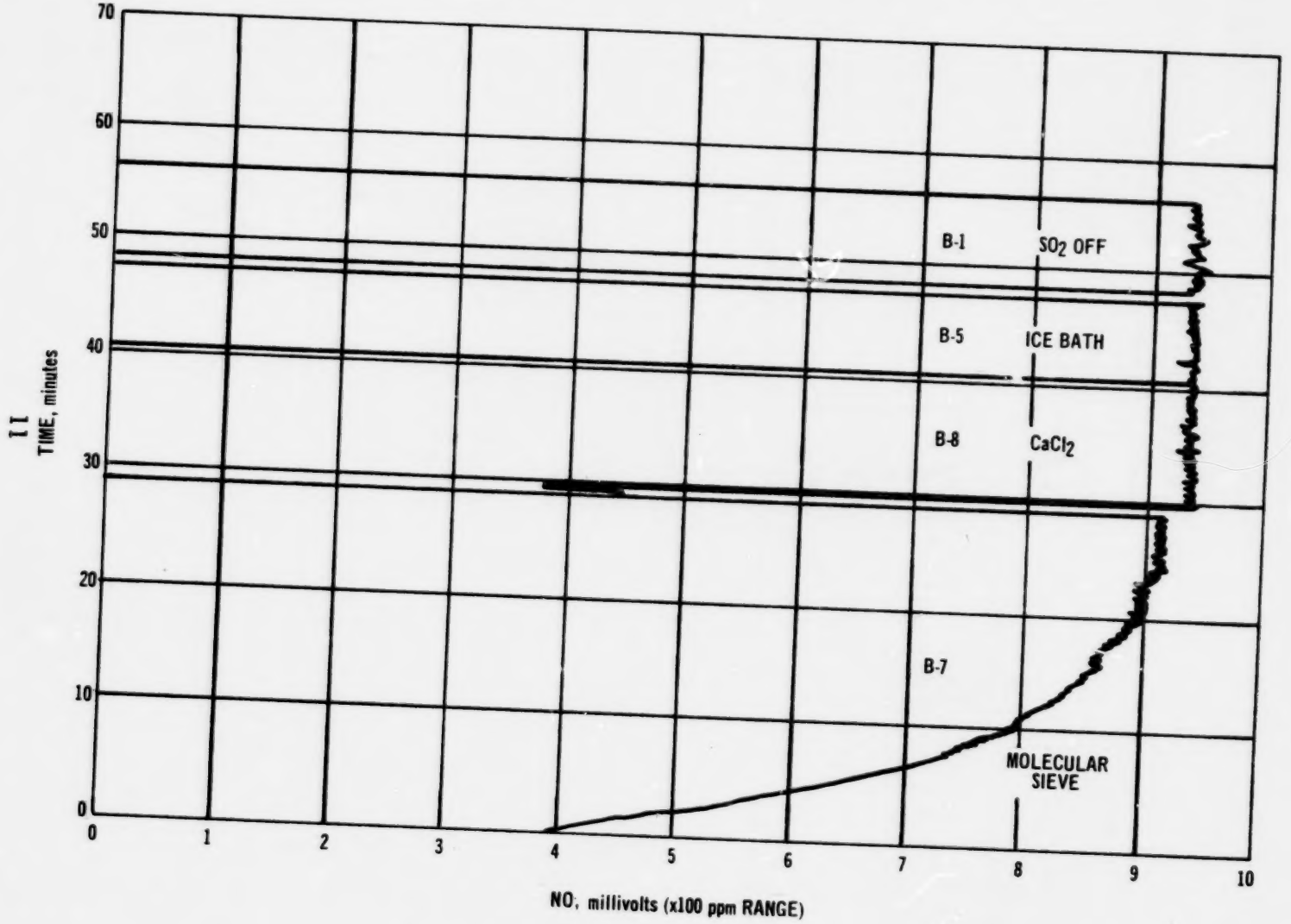

Figure 3. Recorded traces for tests B-1, B-5, B-7, and B-8.

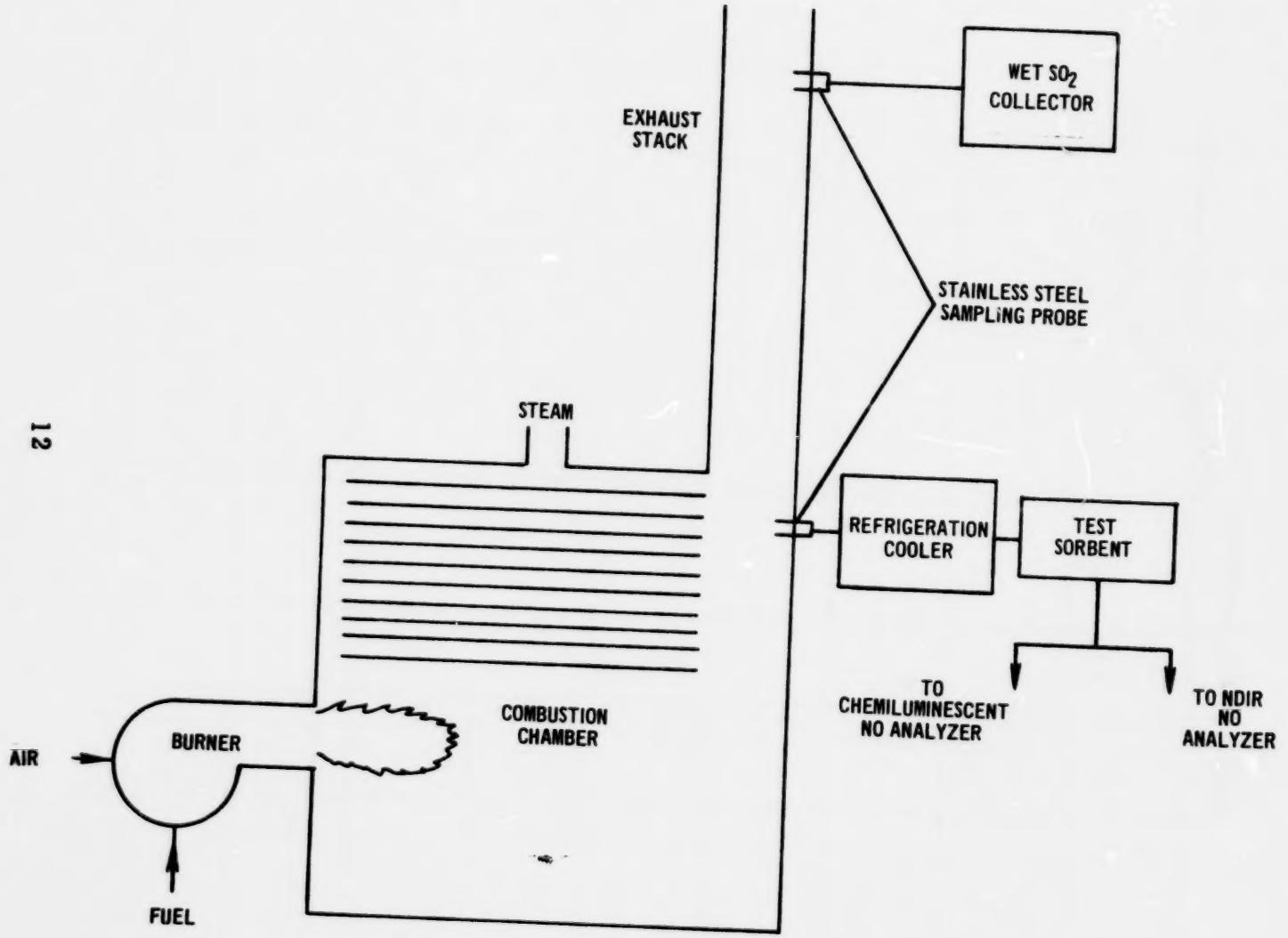

Figure 4. Package boiler hot-flow test facility.

HOT-FLOW TESTING -- RESIDUAL-OIL-FIRED PACKAGE BOILER

The final test series was conducted in a 60-hp residual-oil-fired package boiler. The purpose of this series was to confirm the previous results with flue gas from a typical commercial system and to quantify the actual effects. Figure 4 shows the experimental setup used for this series. Basically, it consisted of a 64-liter/hr (17-gph) Scotch-Marine boiler operating at 25 percent excess air. NO was measured by both chemiluminescent and NDIR analyzers. SO_2 was determined by wet chemical analysis (Shell method[4]). During each experiment the flue gas sample from the boiler stack was passed through a cooler and the test bed before going to the appropriate analyzer.

The results of Tests C-1 through C-5 are shown in Table 3. In Test C-1 no drying agent (other than the refrigeration cooler) was used to remove water vapor prior to the emission analysis. The 232 ppm NO is considered to be the baseline emission for this unit. In the next four tests new and regenerated molecular sieve and Drierite samples were used for final sample drying. (New implies the material had just been received from the manufacturer; regenerated implies the material had been used on several prior occasions for water removal and then "regenerated" by heating to drive off absorbed water.) The data indicate that:

1. With both molecular sieve and Drierite some reduction in NO does occur across the drying material, confirming the Series A and B results.
2. The process involves simultaneous reaction of both NO and SO_2.
3. Regenerated molecular sieve gave the largest reductions in both NO and SO_2.

Table 3. SERIES 3 RESULTS -- EMISSIONS AFTER 5 MINUTES OF SAMPLING[a]

Test No.	Drying agent[b]	NO by chemiluminescent, ppm[c]	NO by NDIR, ppm	SO_2 by wet chemistry,[d] ppm
C-1	None	232	ND[e]	421
C-2	New molecular sieve	138	143	
C-3	Regenerated molecular sieve	99	105	25
C-4	New Drierite	122	185	
C-5	Regenerated Drierite	183	174	

[a] 60-hp residual-oil-fired package boiler at 25 percent excess air.

[b] In all cases refrigeration cooling was used to remove the initial portion of the water.

[c] As measured, dry.

[d] Shell method (for details see Reference 1).

[e] Since water vapor strongly interferes with NDIR analyzers it was not possible to use these analyzers without moisture removal.

It should be noted, however, that eventually the measured emissions approached the baseline level as the drying material "saturated". To quantify this phenomenon three tests were run where flue gas was drawn through 65 grams of regenerated molecular sieve and the emissions were monitored in turn for NO by chemiluminescent analysis, SO_2 by NDIR, and NO by NDIR, all as a function of time. The reduced results are shown in Figure 5. C_t/C_o is the ratio of the concentration of pollutant after a given number of liters of gas had passed through the sieve bed to the correct (baseline) emission level. (Thus a C_t/C_o of 1.0 means no reduction in pollutant concentration is occurring across the bed and a C_t/C_o of 0.0 indicates complete reduction: zero pollutant concentration after the bed.) The data show that for the test case of 65 grams of molecular sieve a 75 percent reduction in SO_2 and a 55 percent reduction in NO occurred for the first 25 to 30 liters of gas. From these data an SO_2 removal of 0.59 mg/g of sieve was estimated; the NO removal was 0.077 mg/g of sieve. The relative volumes also appear to be 3 parts of SO_2 for 1 part of NO.

To investigate the possible use of dry sorption as a possible simultaneous NO_x/SO_x control technique the data were used to estimate a system for a 1000 mw power plant burning 1 percent sulfur fuel. (It should be clearly noted that this type calculation is crude at best because no attempt was made to experimentally optimize conditions, sorbent, bed configuration etc., and all work was done on a very small scale system, 65 grams of material.) The calculations indicated that 5.9×10^6 Kg/hr (13×10^6 lb/hr) of molecular sieve would be required to reduce SO_2 concentration from 421 ppm to <25 ppm and simultaneously reduce NO concentration from 232 ppm to 99 ppm.

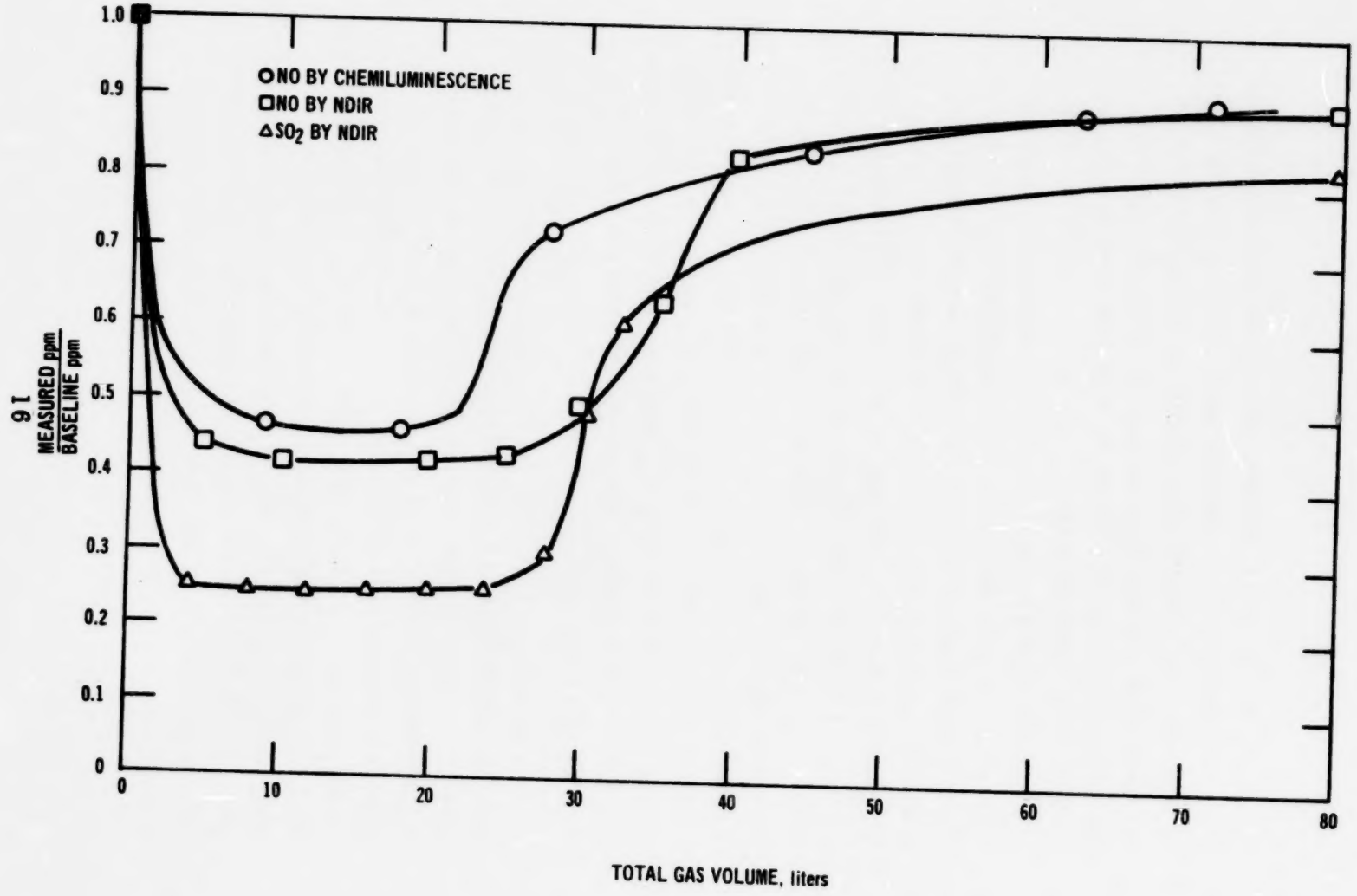

Figure 5. Emission reduction across a 65-gram molecular sieve bed.

CONCLUSIONS/RECOMMENDATIONS

1. Use of a solid sorbent drying material prior to NO analysis can lead to erroneously measured NO concentrations in SO_2 laden flue gases. Drierite and molecular sieve have both been shown to be susceptible to this problem in varying degrees; calcium chloride dehydrate appears to be a possible alternative but needs a more complete analysis. The results are rudimentary at best but even so they suggest the serious need for a detailed chemical-analytical study to provide definitive guidelines for NO_x sampling.

2. Both Drierite and molecular sieve have been shown capable of simultaneous NO and SO_2 "removal" when both are present even in low concentrations. Experimental work should be undertaken to define the fate of the specie; i.e., is the NO being retained on the surface of the sorbent in some form or is it coming through the bed in a form not detected by the analyzer (e.g., NO_2)?

3. Since this concept potentially offers simultaneous NO_x and SO_x removal work should be undertaken to assess the feasibility of using it for flue gas treatment. Future work should develop data on the effect of sorbent composition and structure, NO_x and SO_x concentrations, and regeneration times so that a reasonable economic analysis can be conducted.

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